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Adsorption on Quartz of Co(II), Ni(II), and Cu(II) in the Form of Hydroxide Nanoparticles or Metal Ionic Species from Solutions with pH Close to That of the Onset of Hydroxide Formation

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Abstract—The kinetics of adsorption and desorption of Co(II), Ni(II), and Cu(II) from aqueous solutions were studied at such pH values when the prevailing metal species in the continuous phase is either hydroxide or Me^{2+} (at pH only slightly lower than that at which the hydroxide starts to precipitate). The desorption was performed by methods producing different effects on the adsorbed layer. The time of the preceding adsorption was also varied. A significant difference in the adsorption–desorption behavior of the metals was revealed. This difference cannot be explained without considering the effects related to the detailed electronic structure of metal species and of the adsorbent active centers. The observed trends are attributed to the difference in the properties of the metals as electron pair acceptors and of the surface coordination compounds formed.

Study of regular trends in recovery of transition metal hydroxides with various available oxides is an urgent environmental problem. Its solution largely depends on understanding of interactions of dispersed particles. Both theoretical and experimental aspects of the problem are actively studied. However, certain principal questions are not yet fully understood, in particular, the nature of molecular forces acting in the zone of contact of two particles, related to the specific electronic structure of the surface centers of both particles. In numerous papers, it was suggested to use the concepts of coordination chemistry in studying the specific features of interfacial processes on oxides. In particular, donor–acceptor forces are presumed to exert a decisive effect. This work continues our studies of the regular trends in adsorption and adagulation in systems in which specific features of the electronic structure of participants of surface reactions can be manifested because of the formation of surface coordination compounds (“coordination model of specific adsorption”) [1, 2].

The main goal of this work was to obtain experimental data on the interaction of dispersed particles of quartz and of nanoparticles of 3*d*-transition metal [M(II)] hydroxides [Co(II), $3d^7$; Ni(II), $3d^8$; and Cu(II), $3d^9$] in aqueous solutions. In addition, it was of interest to check with our systems the assumption, repeatedly made in the literature, that, at the pH only slightly lower than the pH of the onset of hydroxide formation (when ionic adsorbate species are still present in the solution), active formation of the hydroxide, followed by polymerization, in the surface layer is quite possible [3].

The interaction of the above components of dispersions was evaluated by the recovery (adsorption) of hydroxides by a quartz dispersion from the aqueous phase and the reverse desorption of hydroxides into the aqueous phase from the modified quartz surface (since the aqueous phase with hydroxide particles looked like a transparent solution, we use the term “adsorption” instead of “adagulation” and the term “desorption” for the reverse process). The Me(II) concentration (c_{Me}) in the aqueous phase, the amount of Me(II) adsorbed by 1 g of SiO_2 (X), and the electrokinetic potential (ξ) served as characteristic parameters; c_{Me} was determined spectrophotometrically with a Specol-10 single-beam spectrophotometer. The Co(II), Ni(II), and Cu(II) concentrations were determined with nitroso-R-salt, PAN [1-(2-pyridilazo)-2-naphthol], and xylenol orange as indicators at wavelengths of 520, 540, and 580 nm, respectively. The X values were calculated from the difference between the metal concentrations in the aqueous phase at the moment of contact and after a certain time, the dispersed phase weight, and the continuous phase volume. The ξ-potentials were calculated from the results

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of microelectrophoretic experiments using the Helmholtz–Smoluchowski equation. The error of spectrophotometric measurements was within 0.5–3%, and the error in determining the ξ-potential, within 5–10%. The errors increased as the above characteristic parameters decreased approaching the detection limit of the spectrophotometric analysis or the zero value of the ξ-potential.

The equivalent diameter of quartz particles d_{eq} in the fraction used in the adsorption–desorption experiment ranged from 40 to 70 μm. The specific surface area (S) of this fraction, determined from the adsorption of nitrogen and methylene blue, was 0.2–0.21 $m^2 g^{-1}$. In the experiments on determining the ξ-potential, the particle size was smaller than 10 μm. According to ultramicroscopic observations, the Ni(II) hydroxide particle size in a freshly prepared dispersion varied within 30–70 nm. As we estimated, the cobalt hydroxide particles had a similar size. The $Cu(OH)_2$ particle size was about 0.5 μm, which was at the limit of observation with the available microscope.

In the experiment, Me(II) could be both in the ionic state and in the form of dispersed hydroxide particles. Strictly speaking, the term "solution" is incorrect in the case of presence of dispersed particles. However, as the presence of the particles is not detected visually, we conventionally term the aqueous phase containing the Me(II) compounds in any form as a "working solution." Working solutions were prepared from Me(II) nitrates (concentration 10^{-4} M); the ionic strength, 10^{-3} M, was the same for all the solutions; two different pH values were adjusted.

The constant ionic strength and the required pH were adjusted by adding KNO_3, KOH, and HNO_3 in appropriate concentrations. In addition to working solutions, we used supporting electrolyte having the same pH and ionic strength as the working solutions but containing no Me(II).

The pH values were chosen so that the most part of Me(II) be in the hydroxide form at a "high" pH and in the mononuclear, same for all metals, form at a "low" pH; the "low" pH was only slightly lower than the pH at which the hydroxides start to actively form. In addition, within the limits of the above requirements, it was advisable to take the same pH for different metals, in view of the fact that the form of the quartz active center $\{[\equiv SiO]^-$ or $[\equiv Si(OH)]^0\}$ is very important for the adsorption. Naturally, when revealing the specific features of different metals, the number of such centers should be as similar as possible.

The speciation diagrams of the metals in aqueous solutions are known [4]. In principle, however, the relative amounts of the hydrolyzed metal species can vary in time after the preparation of solution. For more exact knowledge of the metal speciation, we performed potentiometric titration of working solutions with the age of 1 to 24 h. Our results clearly revealed a change in the speciation during a long storage of the solution. Therefore, in the main experiment, we used only freshly prepared solutions. In accordance with the results of titration, the pH values of 10.5 and 7.3 equally meet the above requirements in the cases of Co(II) and Ni(II). At pH 10.5, 95% of Co(II) and 80% of Ni(II) are in the hydroxide form, the remaining (20%) part of Ni(II) forming the anion $Ni(OH)_3^-$. At pH 7.3, about 95–97% of Co(II) and Ni(II) is in the form of Co^{2+} and Ni^{2+}, and only 3–5%, in the form of the hydroxides. The pH 7.3 is only slightly smaller than the pH of the hydroxide formation for both Co(II) and Ni(II), 7.8 and 8.5, respectively. As for Cu(II), such pH values could not be chosen, because in the pH range of 5.5 to 7.0 several species coexist in comparable amounts, and active hydroxide formation starts at pH 7.2–7.3. Furthermore, the cyclic dimer $[Cu_2(OH)_2(H_2O)_8]^{2+}$, in which the electron density is localized inside the ring, severely complicates the pattern. Theoretically, the bonding of Me with the SiO_2 surface ligand should be appreciably weakened in this case [5–7]. With Cu(II), we chose two pH values limiting the region of active hydroxide formation from above and from below. At pH 10.5, Cu(II) is mainly in the anionic form $[Cu(OH)_3^-]$, and we chose pH 9.0–9.5 as a "high" pH. At this pH, the anionic form content is low (0–10%), and Cu(II) is almost entirely in the hydroxide form. As "low" pH we chose pH 7.3 at which copper also occurs almost entirely in the hydroxide form.

To estimate the kinetics of surface processes, the characteristic parameters were monitored during a prolonged contact of the phases: a working solution and the initial quartz in adsorption or a supporting electrolyte solution and the quartz after the adsorption stage (hereinafter, modified quartz) in desorption. Simultaneously, the pH was measured in solutions over quartz in adsorption and desorption, as well as in the supporting electrolyte solution.

Because of the sensitivity of the surface properties to the surface chemical composition, all the experiments should be performed with the same portion of quartz. We have already published some data for similar systems containing Ni(II) and Cu(II) [7, 8]. However, according to our results of potentiometric titration, quartz used in [8] was essentially different from that in this work. The same can also be true for quartz used in [7]. The quartz portion used in this work was pretreated as follows. Quartz of the Kyshtym deposit (99.8% α-quartz) was ground in a metallic ball mill, washed first with dilute sulfuric acid to remove iron and than with distilled water to neutral reaction of H_2O, fractionated, and dried at 110°C. The resulting powder was kept under distilled water.

The degree of dissociation of active centers on the quartz surface as a function of pH was estimated by continuous potentiometric titration; for description of the procedure, as applied to solutions and dispersions, see [9]. A portion of the quartz powder fraction with $d = 40–50$ μm was dried with a filter paper before the titration, weighed, and suspended in a solution with pH 3. Both the solution and the dispersion contained 10^{-3} M KNO_3. The titration was performed within the range pH 3–10. From the results of the potentiometric titration and the specific surface area, we determined the amount of negative groups $[\equiv SiO]^-$ per unit surface area of quartz (mol m^{-2}): 5×10^{-6} at pH 7.3, 7.2×10^{-6} at pH 9.5, and 8.3×10^{-6} at pH 10.5.

Before starting the adsorption–desorption experiment, a quartz sample was prepared as described above and placed in a supporting electrolyte solution of given pH for 24–48 h, with intermittent replacement of the solution. According to our experience and published data, this time is sufficient for the formation of the electrical double layer if there are no chemical reactions in the dispersion at a given pH. Then the solution over quartz was decanted, quartz was washed with a new portion of the supporting electrolyte solution, and the adsorption–desorption experiment was immediately started.

Adsorption was studied by the static method, and desorption, by three methods differing in the effect on the adsorbed metal layer. The static, dynamic, and electroosmotic methods [8] were used. The static method is the mildest, while the electroosmotic method involves the most severe treatment. Desorption was always performed with supporting electrolyte solutions. The first two methods are hereinafter named traditional methods, as they are frequently used for studying desorption. Apart from our studies [8, 10, 11], the electroosmotic method is discussed only in a few papers, mostly related to the problem of soil compaction and fixation [12].

The dispersions for studying the adsorption of Me(II) contained 2 g of quartz powder and 20 cm^3 of a freshly prepared working solution. The system was hermetically sealed for a time (t_{ads}) specific for each sample. Then the solution was decanted, its pH was measured, the residual metal concentration in the solution was determined, and the modified quartz was used in desorption experiments. In these experiments, we chose the time t_{ads} of 1, 24, and 168 h. When using the static method, the modified quartz was placed in 20 cm^3 of a supporting electrolyte solution of the same pH, hermetically sealed, and worked up by the standard procedure.

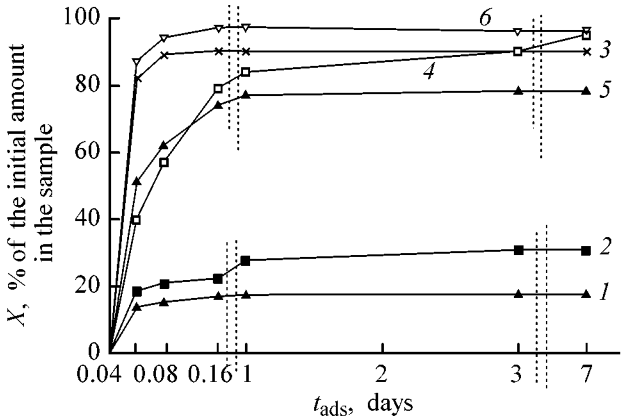

Fig. 1. Amount of adsorbed Me as a function of adsorption time. pH of the initial solution: (*1–3*) 7.3, (*4, 5*) 10.5, and (*6*) 9.5; (*1, 4*) Co, (*2, 5*) Ni, and (*3, 6*) Cu.

When using the dynamic or electroosmotic method, a diaphragm was formed from the modified quartz, and the supporting electrolyte solution was filtered through it at a pressure differential or under the action of a dc electric field, respectively. To compare the effeciency of the Me(II) desorption by electroosmotic and dynamic methods, the experiments were performed at the same flow rate of the supporting electrolyte solution. An electric field of 10 V cm^{-1} was used in electroosmotic experiments. The pressure in the dynamic filtration mode was calculated using the equation of maximum electroosmotic rise [13] derived by replacing Poiseuille’s formula by Darcy’s formula. The amount of the desorbed metal was calculated from the Me(II) concentration in the filtrate and the filtrate volume.

The results of measuring the characteristic parameters of adsorption and desorption and their time dependences are shown in Figs. 1–3.

The course of adsorption of all Me(II) at all the chosen pH values is illustrated in Fig. 1. The Me(II) amount adsorbed from a given volume of the continuous phase is represented in percents of the initial amount in the same volume (X, %) as a function of

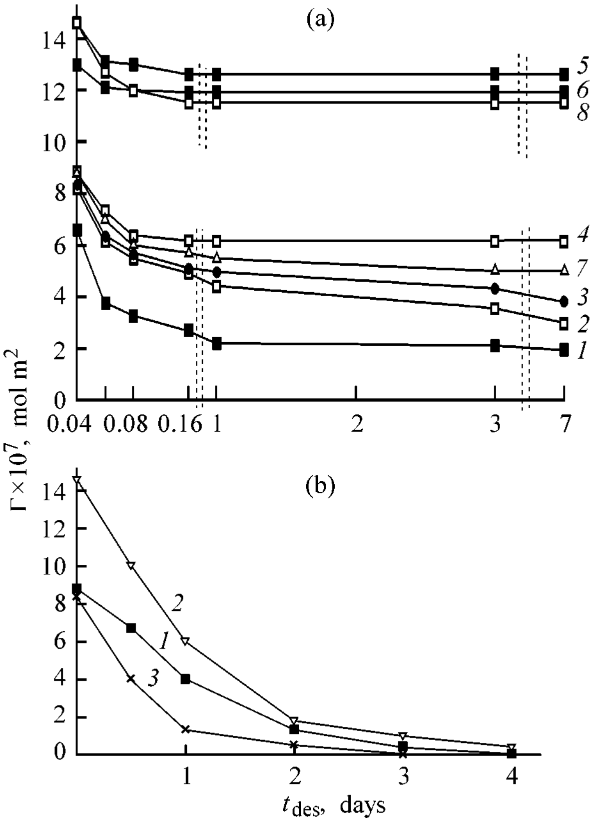

Fig. 2. Amount of adsorbed metal Γ as a function of desorption time t_{des}, with Me(II) in the ionic form. (a) Traditional desorption methods: (*1–6*) static and (*7, 8*) dynamic; (*1–3*) Co and (*4–8*) Ni; adsorption time: (*1, 4, 7*) 1 h, (*2, 5*) 1 day, and (*3, 6, 8*) 7 days. (b) Electroosmotic displacement method: (*1, 2*) Ni and (*3*) Co; adsorption time: (*1*) 1 h and (*2, 3*) 7 days.

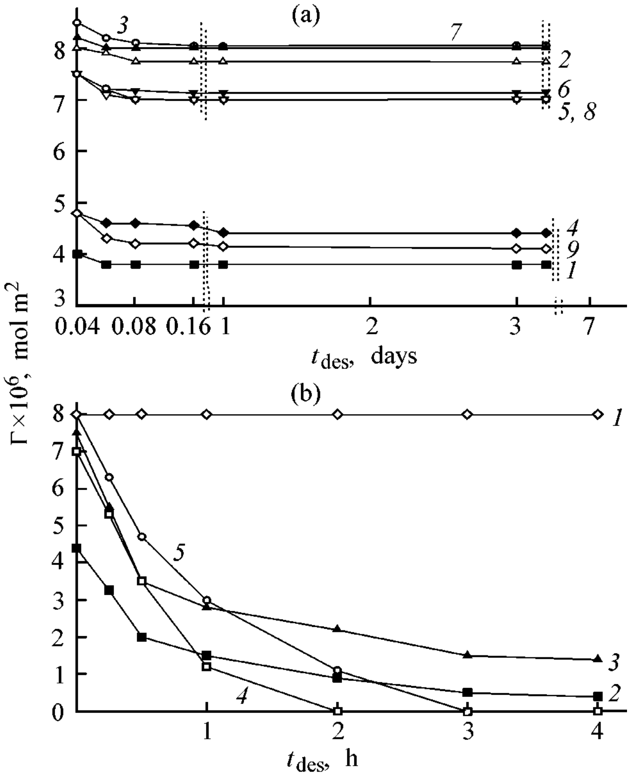

Fig. 3. Amount of adsorbed metal Γ as a function of desorption time t_{des}, with Me(II) in the hydroxide form. (a) Traditional desorption methods: (*1–7*) static and (*8, 9*) dynamic; (*1–3*) Co, (*4–6, 8, 9*) Ni, and (*7*) Cu; adsorption time: (*1, 4, 9*) 1 h, (*2*) 1 day, and (*3, 6–8*) 7 days. (b) Electroosmotic displacement method: (*1*) Co, (*2, 3*) Ni and (*4, 5*) Cu; adsorption time: (*1, 3, 5*) 7 days and (*2, 4*) 1 h.

the time of the phase contact (t_{ads}). Such a choice of units seems to be preferable for practice, as demonstrating the efficiency of adsorption in the limiting cases. The adsorption as the number of moles per unit surface area of adsorbent (Γ, mol m^{-2}) can be readily calculated by

$$\Gamma = Xc_0V_{exp}/mS_{sp},$$

where c_0 is the Me(II) concentration in the initial aqueous phase, V_{exp} is the continuous phase volume, and *m* is the amount of an adsorbent (g) in a given experiment.

The results of desorption are shown in Figs. 2 and 3. Figure 2 refers to the systems where a metal was in the ionic form Me^{2+}, and Fig. 3, to the systems with hydroxide nanoparticles. In adsorption of ions, using the quantity Γ, we can compare the amount of an adsorbed metal (or the corresponding number of positive charges) with the characteristic, for a given pH, number of groups $[\equiv SiO]^-$ on the SiO_2 surface (equal to the number of surface charges of a negative sign). As the recalculation is simple, the use of different dimensionalities in Figs. 1 and 2 will cause no problems in estimating the desorption efficiency. In addition, the Γ values for t_{des} = 0 in Figs. 2 and 3 are directly related to the *X* values obtained at the time when the adsorption stage was finished (t^*_{ads}). Although the particle size, rather than the number of moles of Me(II) per unit surface area, is decisive for estimating the energy of interaction between quartz and hydroxide particles, the choice of the same dimensionality as for the ionic systems is justified by the possibility of quantitative comparison of the desorption data obtained at any pH.

The above results allow the following conclusions.

(1) The adsorption efficiency strongly depends on the speciation of any Me(II) in a working solution. When in the hydroxide form, all the metals were re-

moved from the aqueous phase almost completely. Even at the limiting time of adsorption, the amount of the metal adsorbed in the ionic form did not exceed 35% of the amount of the metal adsorbed in the hydroxide form.

(2) Among the metals occurring in working solutions in the ionic form, Ni^{2+} was adsorbed in approximately two times larger amount as compared to Co^{2+}. With Ni^{2+}, the limiting value of X (plateau) was attained in a considerably longer time (about 48–72 h) than with Co^{2+} (about 1–2 h).

(3) When Co(II) was brought in contact with the solution with pH 10.5, the X value appreciably changed throughout the whole 168-h period, and in all the other cases the curves flattened out. With Cu(II), X attained its limiting value in a shorter time than with Ni(II) [correspondingly, X increased more slowly in the systems with Ni(II) than in those with Cu(II)].

Let us now discuss the desorption data for the ionic form of the metals in solution (Fig. 2). The results obtained with the static and dynamic desorption modes are shown in Fig. 2a. The influence of metal and t^*_{ads} is illustrated by a series of curves related to the static method. The influence of the desorption mode is illustrated by a pair of curves related to one system [in the adsorption stage, the quartz surface was modified with Ni(II) for 168 h]. The following facts are worth noting.

The amount of Me(II) remaining on the adsorbent after desorption depended on t^*_{ads}: $\Gamma_{\text{Co(Ni)}}$ increased with t^*_{ads} at a given desorption time.

At a given t^*_{ads}, Co(II) was desorbed in a considerably larger amount than Ni(II). The Γ value of Co(II) gradually decreased throughout the prolonged desorption experiment, whereas Γ of Ni(II) in the course of desorption reached a certain limit. The desorption efficiency and the kinetic features of desorption performed in the dynamic mode are close to those obtained in the static mode. In the dynamic mode, the amount of retained Ni(II) was 85–87% of the adsorption limit (in the static mode, 90%). For Co(II) at the same t^*_{ads} and desorption time, the difference in the amounts of the adsorbed metal is somewhat larger but also insignificant.

The efficiency of the electroosmotic method is illustrated in Fig. 2b by the results of desorption of Co(II) and Ni(II) from the quartz surface modified for the longest time (168 h). In all the cases, both Co(II) and Ni(II) were desorbed practically completely, both within a fairly short time (0.5 to 2 h).

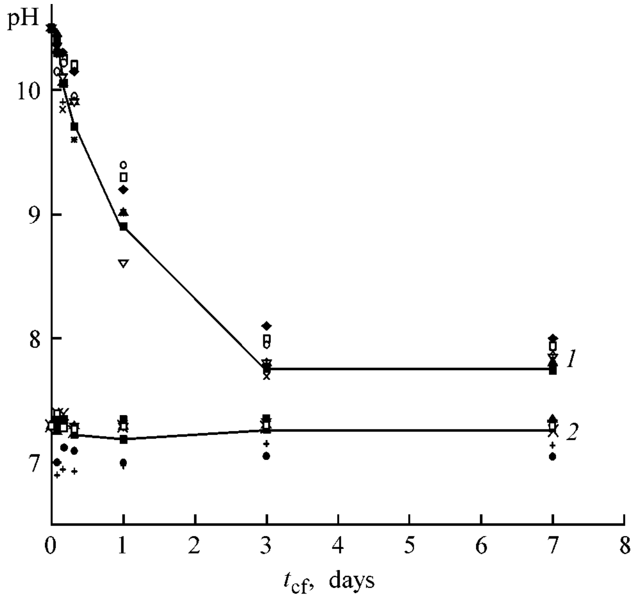

Fig. 4. Solution pH as a function of the contact time t_{cf} of straight (in adsorption) and modified (in desorption) quartz with (*continuous line*) supporting electrolyte and (*points*) working solutions. Six kinds of points correspond to six systems differing in the metal and in the adsorption time. Curve *1* and corresponding points: initial pH 10.5; curve *2* and corresponding points: initial pH 7.3.

Let us now discuss data on desorption in the systems where Me(II) occurred in the hydroxide form (Fig. 3).

The progress of Me(II) desorption with time is shown in Fig. 3a for the static and dynamic desorption modes. Here, as in Fig. 2a, the influence of the metal and t^*_{ads} is illustrated by a series of curves related to the static mode, and only one pair of curves for a single system shows that the choice of a traditional method does not affect significantly the desorption. In the adsorption stage, the quartz surface was modified with Ni(II) hydroxide for 1 h.

As seen from Fig. 3a, there was virtually no desorption, irrespective of the metal and of the adsorption time. We emphasize that this is also true for Co(II).

Fig. 3b shows the results obtained with the electroosmotic displacement method of desorption. The experiments were performed with quartz modified with Me(II) for 168 h. Both Ni(II) and Cu(II) were desorbed completely and fast [Ni(II) was desorbed completely at t_{ads} = 1 h and to 80% at t_{ads} = 168 h]. On the contrary, under the conditions of electroosmotic displacement, there was practically no desorption of Co even after prolonged electroosmotic treatment.

Characteristics of various combinations of particles

Combination of particles	pH	ξ_1, mV	ξ_2, mV	U_{max}, J	$U_{k\,max}$, J
$Co(OH)_2$–$Co(OH)_2$ a_1 25 nm	10.5	–29.5	–29.5	4.9×10^{-20}	5.2×10^{-20}
$Co(OH)_2$–SiO_2 a_1 25 nm, a_2 25 μm	10.5	–29.5	–70.0	4.2×10^{-19}	1.9×10^{-19}
$Ni(OH)_2$–$Ni(OH)_2$ a_1 25 nm	10.5	–33.0	–33.0	6.2×10^{-20}	4.9×10^{-20}
$Ni(OH)_2$–SiO_2 a_1 25 nm, a_2 25 μm	10.5	–33.0	–70.0	4.5×10^{-19}	1.2×10^{-19}
$Cu(OH)_2$–$Cu(OH)_2$ a_1 0.5 μm	9.5	–31.0	–31.0	5.4×10^{-19}	5.2×10^{-19}
$Cu(OH)_2$–SiO_2 a_1 0.5 μm, a_2 25 μm	9.5	–31.0	–70.0	16.7×10^{-19}	8.7×10^{-19}

To conclude, the strength of metal (Co, Ni, Cu) binding on the SiO_2 surface clearly depends on the metal speciation in solution. In case of the hydroxide adsorption, cobalt was fixed on the SiO_2 surface more strongly than nickel and copper. At the same time, data on the adsorption–desorption of the ionic species show that the forces retaining a metal on the SiO_2 surface are appreciably weaker for cobalt than for nickel.

Figure 4 shows how pH varied during a prolonged contact of the initial quartz with working solutions of Co(II) or Ni(II) and with the corresponding supporting electrolyte solutions (in the adsorption stage), as well as during a contact of quartz modified with one of the above metals for 1, 24, or 168 h with the corresponding supporting electrolyte solutions (in the desorption stage).

The following results referring to the adsorption stage should be noted. Irrespective of the metal, the working solution with pH 7.3 became slightly acidified (by approximately 0.4 pH unit) during the first hour. At $t_{ads} > 1$ h, the systems with Co(II) showed no additional changes, while the solution with Ni(II) became slightly alkalized during approximately 72 h. During the contact of quartz with the supporting electrolyte solution at pH 7.3, the pH remained constant within the experimental accuracy. Slight acidification of the working solution within the first hour is most probably due to the exchange of ions in the diffuse part of the electrical double layer (some amount of H^+ is displaced by Me^{2+} entering the electrical double layer). In the systems having the initial pH 10.5, the pH appreciably decreased throughout the period of contact of quartz with both working and supporting electrolyte solutions. We emphasize that the pH values corresponding to each given time t_{ads} were practically independent of whether quartz was in contact with a working or supporting electrolyte solution. In these cases, significant acidification of solutions was caused, in our opinion, by the appreciable solubility of quartz at this pH [14].

From the pH variation in the course of desorption, the following conclusions can be made. In desorption from quartz modified with either cobalt or nickel at pH 7.3 at any t^*_{ads}, the pH is close to that in the systems with the supporting electrolyte solution. In desorption from the quartz surface modified with Me(II) at pH 10.5, the pH appreciably changed in the course of desorption. The pattern was similar to that observed in adsorption. Moreover, the pH values corresponding to any given desorption time t_{des} were virtually equal to those obtained in the adsorption stage at $t_{ads} = t_{des}$ and after the contact of the initial quartz with the supporting electrolyte for the time equal to t_{des}. The t^*_{ads} exerted no influence on the desorption in these systems, as in the systems with pH 7.3.

The table summarizes the characteristics of various pair combinations of particles (a is the average particle radius, the subscripts 1 and 2 refer to the left and right components of a pair, respectively). The particle interaction energies (U_{max}) in the dispersions under consideration, calculated using the classical version of the Deryagin–Landau–Verwey–Overbeek theory (without taking into account the chemical processes in surface layers), are given in the fifth column of the table. The sixth column presents the potential barrier energies ($U_{k\,max}$) in a certain model system consisting of particles with $[\xi] = 30$ mV.[1] It should be noted

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[1] The choice of this ξ value was governed by the occurrence of coagulation at lower ξ, which is a well-known experimental fact [15].

that comparison of $U_{\max}$ with $U_{k\max}$ is rightful if the particles are not subjected to Brownian movement (quartz–quartz interaction). In the case of active Brownian movement, kT is the criterial value of the potential barrier (which is possibly applicable to the interaction between hydroxide particles).

Let us now discuss our results. As noted above, the choice of investigation objects was governed by the assumption that the formation of surface coordination compounds was the cause of specific adsorption of 3*d* elements on oxides. In this connection, we first note that our results disagree with the theories that do not take into account the possible role of surface chemical forces (the theory by Gouy *et al.*). In particular, this concerns our observations that the adsorption–desorption behavior significantly depends on particular M(II) ion (at equal ion charge and equal ξ of quartz). Furthermore, the specific features of particular Me(II) were clearly manifested in the experiments with metals in the hydroxide form, although the hydrolysis constants (pK_h: Co(II) 9.65, Ni(II) 9.86, Cu(II) 8.0) and the molecular weights and ξ values of hydroxides, as well as the Hamacker constants (A_{120}, J: Cu, 2.6×10^{-20}; Ni, 2.2×10^{-20}: Co, 2.0×10^{-20}; n: CuO 2.70, NiO 2.37, CoO 2.2)[2] for all the three metals are close. The size of Co(II) and Ni(II) nanoparticles was also virtually the same.

When interpreting the results in terms of a coordination model, we should take into account general data on the metal coordination behavior in the bulk of solutions, namely, on the acceptor–ligand bond energy, lability, structural form, and type of hybridization of coordination compounds formed in the bulk phase. First, it should be borne in mind that the field of any forces in an aqueous solution region near the interface is strongly nonuniform. The field strength decreases from large values to zero over a distance of up to several tens of nanometers. For example, according to the calculation based on the Gouy theory, the electric field strength in our systems is 10^6–10^5 V cm^{-1} at the dispersed particle surface and zero at a distance of 200–300 nm from the surface. Naturally, such fields should possess a strong polarizing power and should affect the form and stability of a surface complex formed. Second, in heteroligand complexes, the geometry is distorted, which affects their stability. At the same time, with few exceptions, the theoretical information refers to symmetrical homoligand complexes. Therefore, our goal was to show a principal possibility of using coordination-chemical data for analyzing adsorption and desorption in aqueous dispersions quartz–Co(II), quartz–Ni(II), and quartz–Cu(II), rather than to use published data in the literal sense.

The weak fixation of Co in the ionic form in solution is attributable to the generally accepted fact that the Co(II) complexes in any form (as a rule, octahedral complexes are formed) are labile. The strong fixation of Co on SiO_2 at pH 10.5 is attributable to two known facts. First, according to the Pourbaix diagram, there should be no Co(II) hydroxide in equilibrium solutions with this pH, because of ready oxidation of Co(II) to Co(III). Second, Co(III) is one of the strongest acceptors in formation of a donor–acceptor bond. Slow progress of Co(II) adsorption from solution with pH 10.5 is attributable to slow oxidation of the initial Co(II) hydroxide to a Co(III) complex (in solution or in surface layer). This assumption is based on the known inertness of Co(III) complexes. Probably, slow desorption of cobalt from the quartz surface modified by the contact with a solution at pH 7.3 is caused by transformation of a small part of Co^{2+} into Co(II) hydroxide and then into a Co(III) surface complex. The positive effect of the first transformation is in agreement with the basic concepts of the coordination theory of specific adsorption [17], and the occurrence of hydrolysis was presumed in [3]. Such explanation assumes that both transformations should proceed during a certain time.

As for Ni(II), it always remains in the bivalent state. Therefore, the donor–acceptor bond energy could not differ significantly in the cases when quartz was modified in solutions with pH 7.3 and 10.5, in contrast to the systems with Co(II). Data on desorption performed by traditional methods suggest that, for the systems with Ni(II), the donor–acceptor bonds should be the same and relatively strong in all cases. At the same time, these bonds are weaker than the bonds in the surface complex with Co(III), as follows from the comparison of the results of desorption in the electroosmotic mode. The properties of coordination compounds are much more diverse for Ni(II) than for Co(II). For Ni(II), both stable and labile complexes are known, and their geometries can also be different. Taking into account the absence of significant desorption by the traditional methods and the results of some experiments with Co(II) and Ni(II) (see below), we come to a conclusion that, in terms of the coordination model, our data correlate with

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[2] A_{120} is the Hamacker constant of the SiO_2–$Me(OH)_2$ attraction forces in aqueous medium, calculated from published refractive indices n of oxides by the method described in [16]. Unfortunately, the refractive index of CoO is unknown, and we took a value similar to those for CuO and NiO, as many characteristics of these oxides are similar.

the square planar or octahedral structures of surface complexes in the working systems. Such complexes have relatively high energy of ligand field stabilization. It should also be noted that square planar complexes are relatively inert [though more labile than Co(III) complexes], and octahedral complexes are labile. Therefore, we prefer the square planar configuration. Also, although the ligand field stabilization energy in square planar Ni(II) complexes is high irrespective of whether the ligands are strong-field or weak-field, we consider the surface ligands in our working systems to be weak-field ligands. This assumption is based on the comparison of the adsorption–desorption data for Ni(II) and Co(II) obtained with working solutions of pH 7.3. The weak adsorption of Co(II) at the most probable octahedral form of the complex is consistent with the low energy in the case of a weak ligand field, whereas in a strong field the energy should be significant.

In the systems with Cu(II), similar to those with Ni(II), the valence state could not change at changing pH of solution, and complexes of various geometries and energies could form. The absence of appreciable desorption with the traditional methods suggests formation of relatively strong bonds. The known calculations of the ligand field stabilization energy, taking into account that the surface ligands of SiO_2 are weak-field ligands, are consistent with the square planar geometry of the Cu(II) surface complex. The bond energy is close to that in the nickel surface complex.

A slight difference in the amounts of adsorbed metal at the same state of Cu(II) in the aqueous phase is apparently due to variation with pH of the amount of the surface ligand $[\equiv SiO]^-$.

The last question to be discussed is the influence exerted on the adsorption and desorption of the metals by an appreciable change in time of the pH of the working solution with the initial pH 10.5. We believe that this influence, if exists, is small. Such a conclusion is based on a large difference in the amounts of the adsorbed metal in the systems with the initial pH 7.3 and 10.5 at the longest adsorption times, when the pH of the continuous phase of the systems with the high initial pH only slightly differed from 7.3. It follows from this conclusion that formation of a surface coordination compound on a given surface center starts once an adsorbate particle enters the surface ligand field. In other words, the sequence of all the stages of formation of a surface complex is determined by the initial composition of the continuous phase. Subsequent variation in time of pH of the continuous phase does not affect cardinally the pathway of formation of the final complex.

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REFERENCES

1. Tikhomolova, K.P. and Aleksandrova, L.K., *Kolloidn. Zh.*, 1988, vol. 50, no. 1, p. 100.
2. Tikhomolova, K.P. and Tsukanova, V.M., *Zh. Prikl. Khim.*, 1997, vol. 70, no. 3, p. 353.
3. Farley, K.J., Dzomak, D.A., and Morel, F.M., *J. Colloid Interface Sci.*, 1985, vol. 106, no. 1, p. 226.
4. Baes, C.F. and Mesmer, R.E., *The Hydrolysis of Cations*, New York: Wiley, 1976, p. 245.
5. Kukushkin, Yu.N., *Khimiya koordinatsionnykh soedinenii* (Chemistry of Coordination Compounds), Moscow: Vysshaya Shkola, 1985.
6. Basolo, F. and Pearson, R.G., *Mechanisms of Inorganic Reactions. A Study of Metal Complexes in Solution*, New York: Wiley, 1967.
7. Tsukanova, V.M. and Tikhomolova, K.P., *Kolloidn. Zh.*, 1996, vol. 58, no. 5, p. 697.
8. Tikhomolova, K.P., Kufman, Yu.V., and Urakova, I.N., *Zh. Prikl. Khim.*, 2001, vol. 74, no. 8, p. 1258.
9. Ahmed, S.M., *Oxides and Oxide Films*, New York: Wiley, 1972, p. 319.
10. Tikhomolova, K.P., *Elektroosmos* (Electroosmosis), Leningrad: Khimiya, 1989.
11. Tsukanova, V.M., *Cand. Sci. (Chem.) Dissertation*, St. Petersburg: Sankt-Peterb. Gos. Univ., 1996.
12. Zhinkin, G.N., *Elektroosmoticheskoe zakreplenie gruntov v stroitel'stve* (Electroosmotic Stabilization of Soil in Construction Engineering), Leningrad: Stroiizdat, 1966.
13. Grigorov, O.N., Koz'mina, Z.P., Markovich, A.V., and Fridrikhsberg, D.A., *Elektrokineticheskie svoistva kapillyarnykh sistem* (Electrokinetic Properties of Capillary Systems), Moscow: Akad. Nauk SSSR, 1956, p. 91.
14. Gribanova, E.V. and Cherkashina, L.M., *Kolloidn. Zh.*, 1989, vol. 51, no. 6, p. 1069.
15. Zhukov, I.I., *Kolloidnaya khimiya* (Colloid Chemistry), vol. 1: *Suspenzoidy* (Suspensoids), Leningrad: Leningr. Gos. Univ., 1949.
16. Malov, V.A. and Eron'ko, O.N., *Teoreticheskie osnovy nekotorykh metodov pererabotki dispersnykh sistem* (Theoretical Principles of Some Methods for Treatment of Disperse Systems), St. Petersburg: Sankt-Peterb. Tekhnol. Inst., 1994.
17. *Spravochnik khimika* (Chemist's Handbook), Moscow: Khimiya, 1965, vol. 3, p. 781.